Science of the Total Environment 672 (2019) 502–514

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Negative emissions technologies: A complementary solution for climate change mitigation

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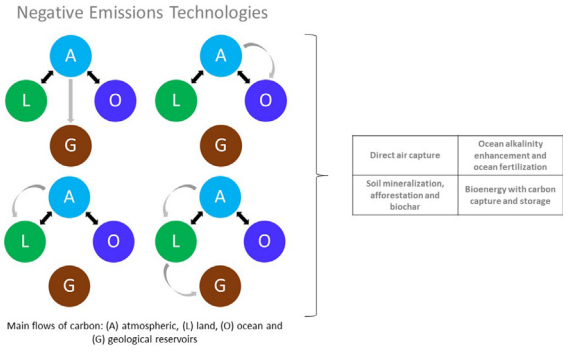
HIGHLIGHTS

- NETs may be required as a complementary solution for climate change mitigation.
- Environmental impacts of a higher scale NETs deployment are crucial.
- Process integration may be performed to reduce the overall cost.
- Power to gas process and microalgal culture should be explored.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 January 2019
Received in revised form 29 March 2019
Accepted 1 April 2019
Available online 2 April 2019

Editor: Huu Hao Ngo

Keywords:
Atmospheric CO_2 concentration
Biochar
Bioenergy with carbon capture and storage
Negative emission technologies
Sustainability

ABSTRACT

Carbon dioxide (CO_2) is the main greenhouse gas (GHG) and its atmospheric concentration is currently 50% higher than pre-industrial levels. The continuous GHGs emissions may lead to severe and irreversible consequences in the climate system. The reduction of GHG emissions may be not enough to mitigate climate change. Consequently, besides carbon capture from large emission sources, atmospheric CO_2 capture may be also required. To meet the target defined for climate change mitigation, the removal of 10 $Gt \cdot yr^{-1}$ of CO_2 globally by mid-century and 20 $Gt \cdot yr^{-1}$ of CO_2 globally by the end of century. The technologies applied with this aim are known as negative emission technologies (NETs), as they lead to achieve a negative balance of carbon in atmosphere. This paper aims to present the recent research works regarding NETs, focusing the research findings achieved by academic groups and projects. Besides several advantages, NETs present high operational cost and its scale-up should be tested to know the real effect on climate change mitigation. With current knowledge, no single process should be seen as a solution. Research efforts should be performed to evaluate and reduce NETs costs and environmental impact.

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https://doi.org/10.1016/j.scitotenv.2019.04.004
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1. Introduction

Since the Industrial Revolution, anthropogenic activities have become the main driver of the global environmental change, shifting the Earth system to an unstable state (Steffen et al., 2007). Rockstrom et al. (2009) identified and quantified planetary boundaries that should not be surpassed to avoid unacceptable environmental changes. Three of nine identified boundaries have been already transgressed due to human action: (i) biodiversity loss; (ii) nitrogen cycle; and (iii) climate change. The latter has taken a high relevance due to the rapid environmental changes: (i) increase of temperature in atmosphere; (ii) decrease of the snow and ice covered regions; and (iii) rise of sea level (Change IPoC, 2013; Dawson et al., 2011; Meinshausen et al., 2009; Whiteley, 2011). These phenomena are related with greenhouse gas (GHG) emissions to atmosphere (and their accumulation), mainly carbon dioxide (CO_2). Its atmospheric concentration has increased by 50% since the Industrial Revolution (270–275 ppm in 1750; 310 ppm in 1950; 408 ppm in 2018) (Allen et al., 2009; NOAA, 2018; Steffen et al., 2007). Consequently, the ocean has absorbed about 30% of the anthropogenic CO_2 emissions, causing its acidification and the associated consequences (e.g. adverse effects on biodiversity) (Doney et al., 2009; Hoegh-Guldberg et al., 2007; Orr et al., 2005). Global CO_2 emissions are about 36 $Gt_{CO2}\cdot yr^{-1}$ (fossil fuels emissions represent 91% of the CO_2 emitted by anthropogenic activities - https://www.co2.earth/global-co2-emissions), which is higher than the uptake value by natural sinks (Le Quere et al., 2018). A positive balance of about 15 $Gt_{CO2}\cdot yr^{-1}$ (equivalent to 4.1 $Gt_C\cdot yr^{-1}$) is associated to an increase of atmospheric CO_2 concentration of about 2 $ppm\cdot yr^{-1}$ (Goeppert et al., 2012; Lackner, 2009). Fig. 1 shows the tendency of the atmospheric CO_2 concentration (NOAA, 2018), showing an annual oscillation (in Northern hemisphere, atmospheric CO_2 levels decrease about 5 ppm during summer and increase about 7 ppm in winter). The atmospheric CO_2 concentration presents the same temporal behaviour of the global mean temperature (see Fig. 2), showing that these phenomena are correlated.

Aiming to reduce the atmospheric CO_2 concentration, many countries decided to reduce the carbon intensity of their economies (Dovi et al., 2009; Meinshausen et al., 2009; Moss et al., 2010; Pires et al., 2011). In the 21st Conference of the Parties (COP21) that occurred in Paris (2015), an agreement was achieved to reduce GHG emissions in order to avoid the increase of global temperature of 2 °C. One of the main commitments was the protection of the forest, maintaining or even increasing this natural sink. One of the short-term solutions to reduce CO_2 emissions is the carbon capture and storage (CCS). This procedure is mainly applied to capture CO_2 from flue gases (4–14%) and the achieved CO_2 enriched stream is then transported to geological reservoirs to be stored. However, about 50% of the CO_2 emissions are from diffuse sources, e.g. aircraft, shipping or automobiles. Moreover, the application of the climate change mitigation actions has been delayed due to the economic interests (high dependence of fossil fuels to get energy). Therefore, taking into account the long residence time in the atmosphere, atmospheric CO_2 capture may also be required (also

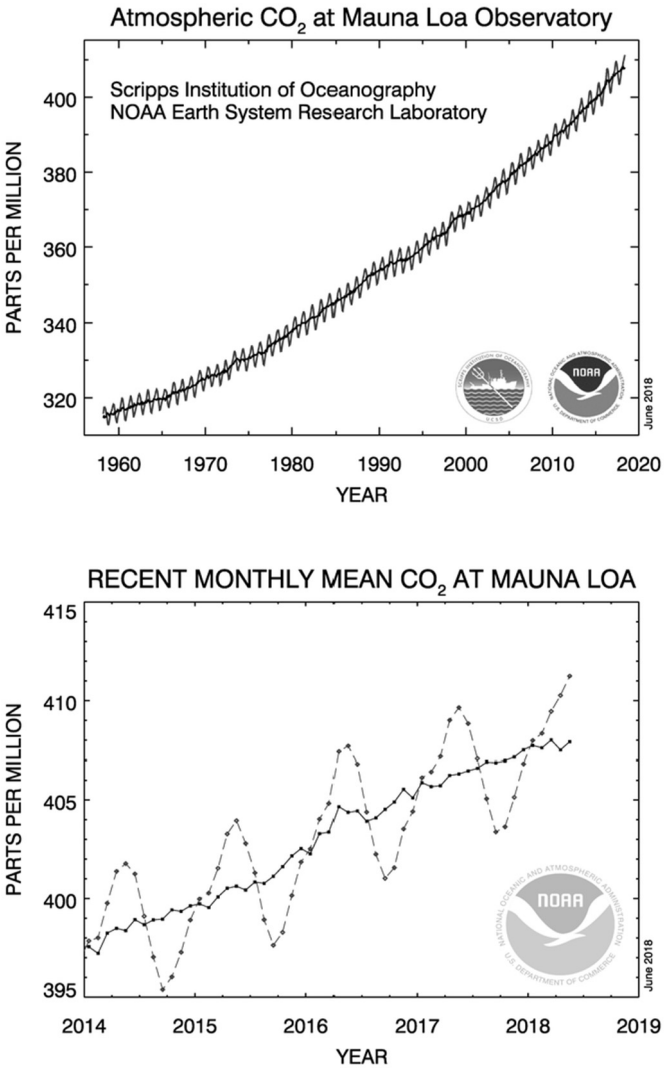

Fig. 1. Global average of monthly mean concentration (in ppm) of atmospheric carbon dioxide for different periods at Mauna Loa Observatory, Hawaii (NOAA, 2018); smooth lines are achieved after correction for the average seasonal cycle.

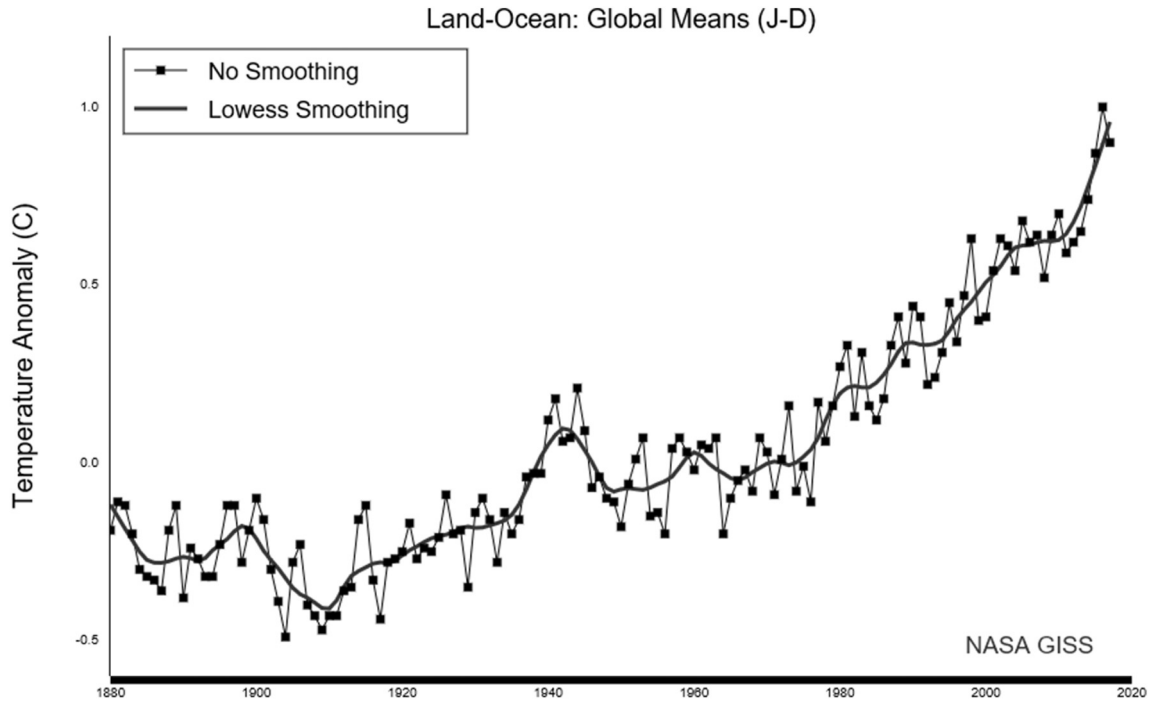

Fig. 2. Air surface temperature anomaly (AST) time series from Goddard Institute for Space Studies (GISS, 2018); smooth lines are achieved after correction for the average seasonal cycle.

known as negative emission technologies – NETs) (Azar et al., 2013; Jones, 2011; Keith, 2009; Lackner and Brennan, 2009; McLaren, 2012; Pielke, 2009). Despite their process drawbacks (CO_2 separation is more difficult, thus involving a higher operational cost), NETs present a set of interesting advantages (Archer et al., 2009; Shepherd et al., 2009): (i) CO_2 capture from any economic activity emitted at different locations and time; (ii) location of the capture unit near the storage site (avoiding the transport costs and its infrastructure); and (iii) the applied separation process is not influenced by other pollutants also emitted by emission point sources (e.g. nitrogen and sulphur oxides), due to their lower atmospheric concentration (Azar et al., 2006; Goeppert et al., 2012; Lackner, 2009; Lackner et al., 2012; Read and Lermit, 2005). Table 1 presents recent research studies with simulated scenarios that showed the need for NETs. However, NETs should be not seen as the solution for the delay of the application of the climate change mitigation policies, but as the complementary solution to the ones defined in COP21. Besides the cost of negative emissions, NETs were not tested at the scale that is modelled in climate scenarios and may not have the required impact on atmospheric CO_2 mitigation (Jones, 2011; Larkin et al., 2018).

The capture of CO_2 from air does not need to extract all the CO_2, but it should collect it as efficiently as possible (typically the economic removal efficiency is less than 50%). This capture cannot be too much expensive, being a reasonable price $30 per ton of CO_2 (Lackner, 2009; Lackner et al., 2012). NETs can be divided in: (i) direct air capture, if physicochemical processes are applied (absorption, adsorption, ocean alkalinity enhancement, and soil mineralization); and (ii) indirect air capture, if biological processes are used (afforestation, ocean fertilization, algal culture, bioenergy with carbon capture and storage - BECCS, and biochar) (McLaren, 2012; Workman et al., 2011). Fig. 3 shows the most important carbon fluxes between atmospheric, land, ocean and geological reservoirs regarding the presented NETs. Table 2 shows some published reviews about different NETs and their focus. This paper aims to present a comprehensive overview of the recent technological advances of the main NETs, presenting also their advantages and drawbacks. Results of main research projects and the economic and technical challenges now and into the future are discussed.

2. Methodology

This study was performed by searching peer-reviewed research papers (until August 2018) using Scopus, Web of Science, ScienceDirect, Wiley and Springer databases by combining the following keywords (and its possible variations): “Zero Carbon Emissions”, “Negative Emission Technologies”, “BECCS”, “Air Capture”, “Direct Air Capture”, “Indirect Air Capture” and “Biochar”. The acknowledgements of those papers were also analysed to search the active research projects in this topic. Then, the information in web sites and reports of these projects were also considered.

3. Direct air capture

The concept of capturing CO_2 from ambient air is not new. This process was already applied in scrubbers for closed environments (e.g. submarines and spacecraft) to reduce the CO_2 concentration to values below 5000 ppm (Lu et al., 2013). As a climate mitigation option, Lackner was the first one to propose in 1999. However, atmospheric CO_2 capture requires high energetic demand, mainly to promote the movement of high amount of air through the scrubber, although wind can be used as air transport. As it is not economically viable to apply a significant amount of energy (heat and work), many separation processes that are applied to CO_2 capture from high concentrated streams (flue gases) cannot be considered in air capture. Below, direct air capture methodologies applied for atmospheric CO_2 are presented: (i) absorption; (ii) adsorption; (iii) ocean alkalinity enhancement; and (iv) soil mineralization. Table 3 presents some relevant issues in research studies regarding direct CO_2 capture.

3.1. Absorption

Absorption is a physicochemical process in which compounds are dissolved in a liquid phase (Pires et al., 2011). The main difference from adsorption is that these compounds are retained in the liquid volume, not on the solid sorbent surface (adsorption). CO_2 absorbents are monoethanolamine (MEA) and strong bases, such as calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH), and potassium hydroxide

Table 1
Recent scenario modelling studies.

NET	Relevant issues	Reference
BECCS	Evaluation of the role of power generation from bio plants with CCS to achieve a low climate target by 2100 using the optimization model TIAMFR (TIMES Integrated Assessment Model France). Global and regional analyses to quantify BECCS potential in industrialized, fast-developing and developing countries. High dependence of BECCS as a negative emissions process technology on the future development of CCS technology.	Selosse and Ricci (2014)
BECCS	Assessment of economic and deployment implications for BECCS in the electricity system of western North America under aggressive time frames and carbon emissions limitations (SWITCH optimization model).	Sanchez et al. (2015)
All	Quantification of the conventional mitigation and negative emissions required for RCP2.6 (IPCC scenario likely to limit the global warming below 2 °C) based state-of-the-art carbon–climate models. In the best-case, negative emissions of 0.5–3 $Gt_C \cdot yr^{-1}$ and storage capacity of 50–250 Gt_C are required; In the worst case, those requirements are 7–11 $Gt_C \cdot yr^{-1}$ and 1000–1600 Gt_C, respectively.	Gasser et al. (2015)
BECCS	Modelling of a zero emissions scenario based on the A1T scenario of IPCC-SRES. Results suggested that zero emissions scenario may be possible in this century. Energy supply structure (with BECCS) under the zero emissions scenarios was described.	Tokimatsu et al. (2016)
All	Impact assessment on the global carbon cycle across different time horizons, considering different balances of emissions and fluxes, and the responses of the natural carbon cycle. CMIP5 model simulations to quantify how the Earth system may respond to NETs.	Jones et al. (2016)
All	Projection of energy and land-use emissions mitigation pathways through 2100. Anthropogenic emissions need to peak within the next 10 years, to maintain realistic pathways to meeting the COP21 emissions and warming targets. Fossil fuel consumption will probably need to be reduced below a quarter of primary energy supply by 2100.	Walsh et al. (2017)
BECCS	Development strategy of low carbon scenarios that consider interaction of economically viable bioenergy and/or BECCS technological flow, biophysical limit of bioenergy productivity and food security. Evaluation of several bioenergy feedstock and conversion technologies with and without CCS with GRAPE (Global Relationship Assessment to Protect the Environment).	Kato et al. (2017)
Afforestation BECCS	Evaluation of alternative options to greatly reduce the volume of CO_2 removal (CDR) from atmosphere to achieve the 1.5 °C goal. Almost all scenarios still rely on BECCS and/or reforestation. Investment in the development of CDR options remains an important strategy if the international community intends to implement the Paris target.	van Vuuren et al. (2018)

BECCS – bioenergy with carbon capture and storage; IPCC - Intergovernmental Panel on Climate Change; NET – negative emissions technology.

(KOH). MEA is the most used sorbent in CO_2 capture in flue gases. However, the corrosion is its main problem (Goeppert et al., 2011). Thus, these amines are generally used in 20–30% concentration in water. These procedure increases the energetic demand in regeneration step (stripping) due to the high heat capacity of these aqueous solutions. Moreover, these sorbents present lower stability in the presence of air. Air moisture is one the most important problem in absorption process for atmospheric CO_2 capture. Inagaki et al. (2017) evaluated the modification of alkylamines with hydrophobic phenyl group to increase their selectivity between CO_2 and water. Additionally, the tested xylylenediamines were able to capture CO_2 without hydration, reducing the energy requirements for recovery of the absorbent.

CO_2 capture can be also performed by wet scrubbing systems based on cycling technologies using strong bases (Baciocchi et al., 2006; Keith et al., 2006; Zeman, 2007). CO_2 is then recovered by calcination, pressurized and stored. The most studied sorbents are sodium and calcium hydroxide. NaOH solution presents some advantages over $Ca(OH)_2$ (Stolaroff, 2006): (i) lower vapour pressure, reducing water loss; (ii) high hydroxide concentrations enhancing CO_2 capture kinetics; and (iii) reduced probability of accumulation of solid carbonates. NaOH spray-based contactor was studied for air capture, aiming to estimate the costs of a capture unit with this system (Stolaroff et al., 2008). In this process, water loss is significant (20 mol H_2O per mol of CO_2 at 15 °C and 65% relative humidity), which can be lowered by optimizing the system design and operating conditions. The determined cost for the full-scale system is $96\$ \cdot t_{CO2}^{-1}$ in the base case, which can vary between 53 and $127\$ \cdot t_{CO2}^{-1}$ depending of the operating parameters and the assumptions concerning capital cost and mass transfer kinetics. The total energy requirement was from 190 to 390 $kJ \cdot mol^{-1}$ for the tested conditions.

Keith et al. (2006) developed the lime/soda process for CO_2 capture (see Fig. 4). Firstly, atmospheric CO_2 is absorbed in NaOH solution forming sodium carbonate (Na_2CO_3) in a scrubbing tower. Then, Na_2CO_3 solution reacts with $Ca(OH)_2$, generating NaOH (returning to scrubbing tower) and calcium carbonate ($CaCO_3$), which precipitates. This regeneration process (Kraft chemical recovery process) is already applied in pulp and paper mills and other industries. After filtering, $CaCO_3$ is converted to lime by calcination reaction. To increase the purity of CO_2 gaseous stream, this reaction can be performed in a CO_2 environment. The estimated cost was $500\$ \cdot t_C^{-1}$ ($140\$ \cdot t_{CO2}^{-1}$). Process intensification should be perform to decrease the overall cost to 40–80 $\$ \cdot t_{CO2}^{-1}$. One of the drawbacks of this process is the significant water loss due to the high amount of air pumped to scrubbing tower. Moreover, the process presents a significant energy (mainly for pumping) requirements: between 30 and 88 $kJ \cdot mol^{-1}$ (Zeman, 2007). To reduce costs, the scrubbing tower should be designed with large cross-section area to decrease the height of the liquid absorber level (reducing the pressure drop of gaseous stream in the scrubbing tower). Baciocchi et al. (2006) also studied lime/soda process for CO_2 capture. The authors assessed two process designs and total net heat requirements for two different process configurations, achieving the values of 5.3 and $2.6\ GJ \cdot t_{CO2}^{-1}$. Zeman (2007) also performed energy and material balances of this process for CO_2 capture from atmosphere. The energy consumption was calculated as 350 $kJ \cdot mol^{-1}$ of captured CO_2 (mainly thermal energy for calcination and mechanical power for air movement), lower than the values achieved by other authors (Baciocchi et al., 2006; Keith et al., 2006).

3.2. Adsorption

In absorption processes, the thermal energy demand in regeneration step is the main disadvantage. Thus, CO_2 capture in solid adsorbents (physical adsorption) was also studied as an alternative (Belmabkhout et al., 2010; Goeppert et al., 2011; Jones, 2011; Lu et al., 2013). Zeolites, activated carbon and alumina have low CO_2 adsorption capacities, being not considered in air capture. Amines immobilized in solid supports are characterized by lower regeneration temperatures, being also considered a potential solution for atmospheric CO_2 capture (Goeppert et al., 2011; Wurzbacher et al., 2011). These materials have other interesting characteristics, such as a high specific surface area, high CO_2 selectivity at diluted concentrations and tolerance to moisture. The tolerance to moisture is an important characteristic when compared with zeolites in which CO_2 selectivity decreases in the presence of water. Table 4

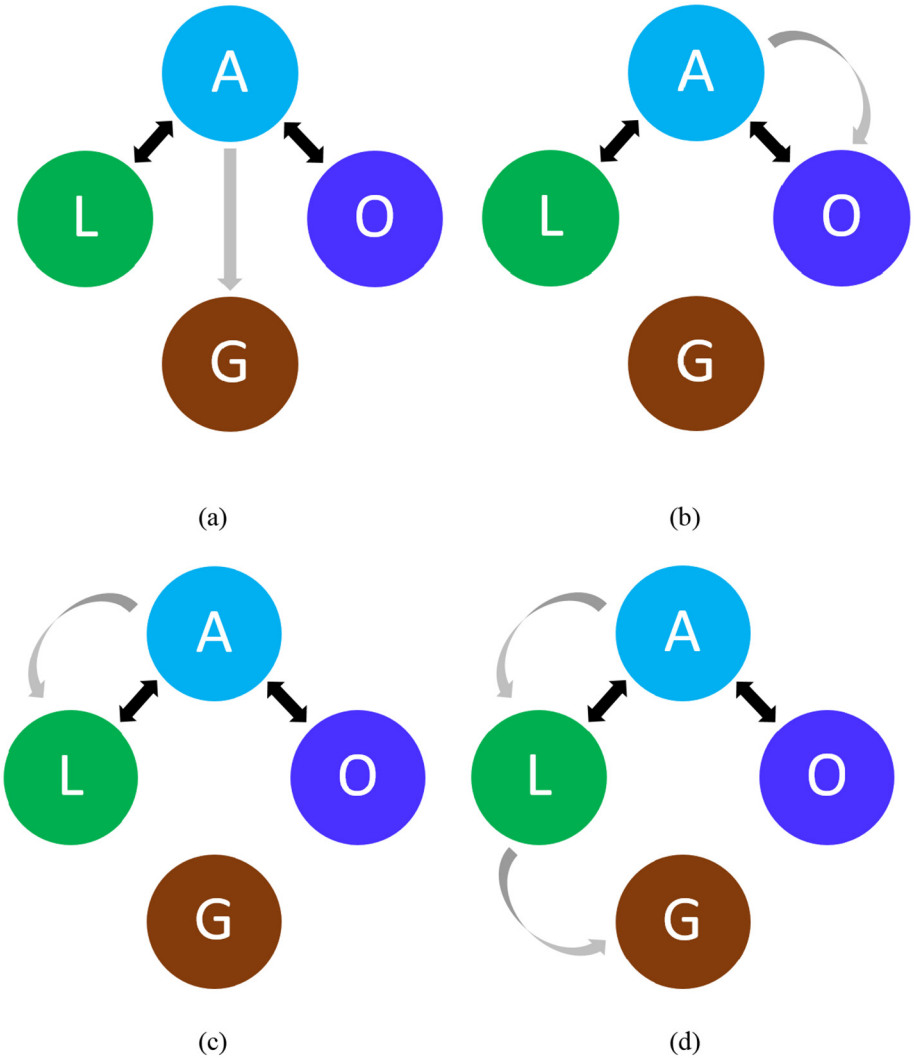

Fig. 3. The main flows of carbon (gray arrows denote carbon removal through NETs) among atmospheric (A), land (L), ocean (O) and geological reservoirs (G): (a) direct air capture (through absorption and adsorption); (b) ocean alkalinity enhancement and ocean fertilization; (c) soil mineralization, afforestation and biochar (addition to soil); and (d) bioenergy with carbon capture and storage (Smith et al., 2016).

shows the main results of different adsorbents when applied for atmospheric CO_2 capture.

Goeppert et al. (2011) evaluated the atmospheric CO_2 capture through a polyamine based solid adsorbent. The moisture effect on the adsorption capacity was studied at room temperature and the regeneration of the adsorbent after adsorption/desorption cycles. The determined adsorption capacity was 1.74 $mmol \cdot g^{-1}$, which was greater than the reported value for the hyperbranched aminosilica adsorbent (1.44 $mmol \cdot g^{-1}$). This study showed that adsorbent based on supported amines are promising low cost materials for CO_2 capture from air.

An emerging material for CO_2 capture is metal-organic frameworks (MOFs), which are crystalline materials consisting of coordination bonds between transition metal cations (e.g., Al^{3+}, Cr^{3+}, Cu^{2+}, or Zn^{2+}) and multidentate organic linkers (e.g., carboxylate, pyridyl) in a three-dimensional network with uniform pore diameter often in the range 3 to 20 Å (Mazzotti et al., 2013). These materials can also be used for gas storage, catalysis and sensing applications. Shekhah et al. (2014) tested MOFs with pore of 3.5 Å for low concentration CO_2 capture. MOF structure was characterized by optimal CO_2 energetics (allow reversible physical adsorption-desorption) and a pore size suitable for direct air capture. In the tested CO_2/N_2 gas mixture, CO_2 apparent selectivity at 1000 ppm CO_2 was not affected by the presence of humidity through the analysis of breakthrough tests.

Besides geological storage, the captured CO_2 can be applied in chemical synthesis processes, e.g. power to gas conversion (Schiebahn et al., 2015; Veselovskaya et al., 2017). With the increase of renewable energy (wind and solar) integration in the electrical grid, the variability of power supply increased and is difficult to predict; thus, this fact puts in risk the electrical grid stability. Consequently, there is an increasing need to find a technology that allows the storage of the excess of electricity produced by fluctuating energy sources. Veselovskaya et al. (2017) evaluated the CO_2 capture from air using a sorbent based on composite material K_2CO_3/Al_2O_3 in temperature swing adsorption (TSA) cycles. The combination between air capture and methane production through Sabatier process (commercial nickel catalyst NKM-2V) was implemented with a two reactor system, presenting high experimental conversions of desorbed CO_2 to methane.

3.3. Ocean alkalinity enhancement

The planet has natural carbon sinks (regions where CO_2 is removed from atmosphere) and sources (carbon is released back to atmosphere) – see carbon flows in Fig. 3 with black colour. Ocean represents the main carbon sink, removing about one third of the anthropogenic emissions from the atmosphere. CO_2 is absorbed in water and reacts with ocean minerals, which help to neutralize ocean acidification. However, the increase of CO_2 emissions creates an unbalance on this system, as oceans

Table 2
Review papers about NETs.

NET	Aims	Reference
Absorption/adsorption	Recent advances in solvents, adsorbents, and membranes for post-combustion CO_2 capture. Review of the concept of extracting CO_2 directly from ambient air as a means of reducing the global atmospheric CO_2 concentration and comparison with post-combustion process.	Jones (2011)
Algal culture	Holistic detailed overview of the process of carbon sequestration, focusing biological carbon mitigation. Assessment of the commercial applications of microalgal biomass from microalgae. Technical barriers (environmental concerns) and economic matters to be overcome.	Farrelly et al. (2013)
BECCS	Overview of BECCS at the systems level, based on relevant information from the recent 5th Assessment Report (AR5) of IPCC. Role assessment of BECCS in stabilising atmospheric CO_2 concentrations. Not address or discuss specific BECCS capture technologies, their technical optimization and RD&D requirements.	Kemper (2015)
Adsorption	Systematic analysis focusing the key technical parameters required for CO_2 capture using physical adsorbents. Recently developed class of MOF adsorbents represent a breakthrough finding for CO_2 capture in diluted streams using physical adsorption.	Belmabkhout et al. (2016)
Absorption/adsorption	Historical overview of the field of direct air capture with extensive description of the chemical sorbents application. New materials need to be further investigated and developed with a practical sorbent−air contacting process.	Sanz-Perez et al. (2016)
Biochar	Assessment of the effect size of biochar amendment on soil CO2 fluxes, SOC, and MBC contents. Key factors influencing the response of soil CO_2 fluxes, SOC, and MBC to biochar amendment.	Liu et al. (2016)
Soil mineralization	Review of the potential of enhanced weathering (EW), applying crushed reactive silicate rocks (such as basalt) on tropical agricultural and tree plantations to offset fossil fuel CO_2 emissions. Identification of nine priority research areas in the topic.	Edwards et al. (2017)
All	Scientometric methods and topic modelling to identify and characterize the available evidence on NETs as recorded in the Web of Science.	Minx et al. (2017)
All	Comprehensive and systematic assessment of the academic literature on NETs. Potential role of NETs for reaching the international climate goals. Costs, potentials, and side-effects for these technologies. Innovation and scaling challenges required for NETs deployment.	Fuss et al. (2018); Minx et al. (2018); Nemet et al. (2018)

BECCS – Bioenergy with carbon capture and storage; IPCC - Intergovernmental Panel on Climate Change; MBC – microbioal biomass carbon; MOF - metal–organic frameworks; NET – negative emissions technology; SOC – soil organic carbon.

do not have such high capacity to absorb (and neutralize) all emitted CO_2, leading to the change in pH levels in ocean surface water.

The addition of alkaline nature compounds (e.g., CaOH, $Ca(HCO_3)_2$) to ocean surface water can enhance the removal of CO_2 from atmosphere and increase of total ocean CO_2 storage (Rau, 2011; Rau and Caldeira, 1999; Renforth and Kruger, 2013). This procedure may have a strong impact on the chemistry of the surface waters (with unknown consequences to the marine environment), requiring detailed studies before its implementation. Moreover, there are also concerns about the impact of massive land-based mineral extraction, processing and transportation (Rau, 2014). Renforth et al. (2013) presented the engineering challenges of the ocean liming. Through a techno-economic analysis, the authors determined that 1.4–1.7 t of limestone is required to remove 1 t of atmospheric CO_2, being needed 0.6–5.6 $GJ \cdot t_{CO2}^{-1}$ of thermal energy and 0.1–1.2 $GJ \cdot t_{CO2}^{-1}$ of electrical energy. Analysing the costs of the process, ocean liming may require 72–159$ $\cdot t_{CO2}^{-1}$. Paquay and Zeebe (2013) applied carbon-cycle model LOSCAR to analyse the effect of ocean alkalinity enhancement in its pH and atmospheric CO_2 concentration for the period between 2020 and 2040. Ten carbon emission scenarios were simulated. These authors also calculated the required amount of CaO and the correspondent cost to maintain the ocean pH above 8.

3.4. Soil mineralization

Soil contains over 2000 Gt_C (the greatest land-based reservoir for carbon in the planet) and the covering vegetation captures up to 3 $Gt_C \cdot yr^{-1}$, representing an important earth carbon sink (Farrelly et al., 2013). The CO_2 exchange between soil and atmosphere is three times higher than the exchange between the ocean and atmosphere. Soils can sequester atmospheric CO_2 by three ways (Lackner, 2002): (i) accumulation of organic carbon resulting from plant growth (representing a fragile stock as the degradation occurs at a rate depending on the storage environment); (ii) rock weathering (promoting the dissolution of inorganic carbon in soil solution); and (iii) precipitation of carbonate materials (stable carbon sink). The enhancement of CO_2 uptake in the soil is a form of carbon abatement that is inexpensive, as it is a passive process (low energy input – similar to the construction of wetlands for treatment of polluted waters). The potential CO_2 removal by enhanced weathering (addition of carbonate or silicate minerals to soils to increase carbonation process kinetics) was estimated to be about 1 $Gt_C \cdot yr^{-1}$ in 2100 (Kohler et al., 2010). The observed climate change has a complex interaction with soil response regarding carbon mineralization kinetics (Keller et al., 2004; Krevor and Lackner, 2011; Qafoku, 2015). Besides the high atmospheric CO_2 concentrations and temperature increase, intense rainfall increase the extent and rates of carbonation by removing the reaction products (by surface runoff or percolating water). Heat waves and droughts may also promote the CO_2 removal, as these phenomena changes the physical properties of rocks and minerals.

4. Indirect air capture

Currently, the natural processes of atmospheric CO_2 capture are mainly based on biological processes. Nature converts CO_2 into organic carbon (carbohydrates, cellulose and lipids) by photosynthesis (producing also oxygen) in plants, trees and algae. For instance, photosynthesis process in the ocean captures about 40% of the atmospheric CO_2 (Goeppert et al., 2012; Pires et al., 2012; Watanabe and Kuwae, 2015). In addition, these processes were responsible for the stabilization of atmospheric CO_2 concentration (280 ppm) during a long time period before the industrial revolution (Pielke, 2009). The enhancement of these natural processes of CO_2 capture has an important advantage against the direct air capture methods, regarding energy requirements. While biological processes uses direct solar energy in CO_2 fixation, the physical and chemical processes requires heat or electrical energy (McLaren, 2012). Moreover, the CO_2 storage is costly and the long term sequestration is not guaranteed (Farrelly et al., 2013; Pires et al., 2011). However, photosynthesis presents lower efficiency in the conversion of solar into chemical energy (most crops present efficiencies between 0.5 and 2%), when compared to solar cells to produce electricity. In the next sections, the main indirect air capture processes are described: (i) afforestation;

Table 3
Direct air capture studies.

NET	Relevant issues	Reference
Absorption	Test of hydrophobic phenyl group into alkylamines of CO_2 absorbents (improved selectivity between CO_2 and water).	Inagaki et al. (2017)
	Evaluation of a NaOH spray-based contactor for use in an air capture system by estimating the cost and energy requirements	Stolaroff et al. (2008)
	Experimental investigation into the combined sodium/calcium capture process.	Zeman (2008)
	Energy and Material Balance of soda/lime process for CO_2 capture.	Zeman (2007)
Adsorption	Characterization of adsorption kinetics of a novel moisture swing process for air capture.	Wang et al. (2016)
	Transient heat and mass transfer model for the desorption step of a temperature–vacuum swing adsorption for air capture.	Wurzbacher et al. (2016)
Ocean alkalinity enhancement	Effect of ocean alkalinity on carbon sequestration.	Renforth and Henderson (2017)
	Assessment of ocean liming consequences and costs.	Paquay and Zeebe (2013)
Soil mineralization	Passive Sequestration of Atmospheric CO_2 through Coupled Plant-Mineral Reactions in Urban soils.	Manning and Renforth (2013)

(ii) ocean fertilization; (iii) algal culture; (iv) bioenergy with carbon capture and storage; and (v) biochar. Table 5 presents some relevant issues in research studies regarding indirect CO_2 capture.

4.1. Afforestation

Afforestation can be also considered a NET, as the forests can safely store several amounts of carbon sequestered by photosynthesis during a long period (Boucher et al., 2012; Obersteiner et al., 2010). From all the CO_2 mitigation options, forest and soil management are the most ready techniques. The increase of forest area by planting new forests or better management of the current natural and plantation forests will improve the carbon sequestration (Shepherd et al., 2009). Biomass provides four routs for CO_2 capture: (i) CO_2 capture and storage in biological form (soil organic carbon and carbon accumulated in plants); (ii) remote storage by biomass harvesting and application (not for combustion processes – e.g. furniture and construction materials); (iii) energy production, reducing the dependence on fossil fuels (biomass represents only 1% of the world generated power); and (iv) energy production with remote CO_2 sequestration (BECCS – power production with post-combustion CO_2 capture and geological storage).

The atmospheric carbon capture by afforestation and reforestation is stored in living biomass. However, the deforestation and the conversion of the land to agriculture practices affect the soil organic carbon stock, causing the release of 20 to 50% of the soil carbon to the atmosphere (Wei et al., 2014). Kindermann et al. (2008) estimated that 50% reduction in deforestation may avoid emissions of 1.5–2.7 $Gt_{CO2} \cdot yr^{-1}$ in the period from 2005 to 2030. Therefore, the success of atmospheric CO_2 capture with this technique depends of long-term forest management (and forest fire mitigation).

Afforestation may have a strong impact in other earth systems. Regarding land use, the CO_2 removal of 1.1–3.3 $Gt_{CO2} \cdot yr^{-1}$ may require 320–970 million hectares of land (Smith et al., 2016). Moreover, high nutrient (nitrogen and phosphorus) requirements were also estimated in the same study. Besides carbon uptake, forestry influences the climate through albedo changes, emissions of volatile organic compounds and microbes (Ellison et al., 2017). Additionally, captured carbon is vulnerable to changes of political priorities, illegal logging (the main contribution to current rates of deforestation), fires, pests and diseases. The current trend of global temperature leads to drying soils and vegetation (water availability/requirements may be an important limit for forest protection), increasing the probability of occurrence of forest fires (recently in several European countries, USA and Australia). Besides destroying the ecosystems (and sometimes loss of human lives), forest fires are responsible for the emission of large quantity of CO_2 that was captured during a long period. Thus, the low security of carbon stored in living biomass requires policy measures to protect and expand the forest. One policy decision that could help in forest protection is the allocation of carbon credits to their preservation (Shepherd et al., 2009).

The afforestation may also enhance the soil organic carbon (SOC), which has an extended mean residence time: 50 to 80 years (Lorenz and Lal, 2014a; Lorenz and Lal, 2014b; Schmidt et al., 2019). Thus, it can have an important contribution on CO_2 capture from air. On the other hand, for agricultural soils, SOC is dependent on the applied agronomic practices (Lal et al., 2004; Marland et al., 2003). The capacity of

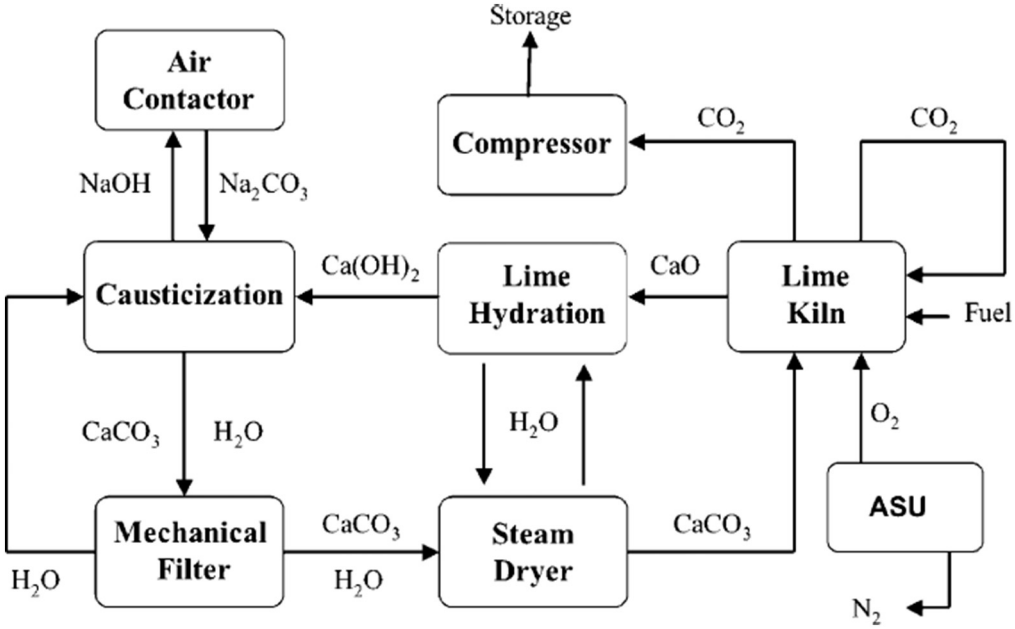

Fig. 4. Soda/lime process for CO_2 capture (Zeman, 2008).

Table 4
Atmospheric CO_2 capture based on adsorption process.

Sorbent	Experimental setup	Sorption capacity	Energy consumption	Reference
Amine-based nanofibrillated cellulose	$[CO_2] = 506$ ppm; RH = 40%; $T_a = 25$ °C; $T_d = 90$ °C; ADP - 2 h/1 h.	SAC = 1.39 $mmol_{CO2}\ g^{-1}$; DAC = 0.695 $mmol_{CO2}\ g^{-1}$	n/a	Gebald et al. (2011)
Amine-bearing mesoporous silica	$[CO_2] = 400$ ppm; RH = 27%; $T_a = 25$ °C; ADP – n/a.	SAC = 0.98 $mmol_{CO2}\ g^{-1}$; DAC = 2.04 $mmol_{CO2}\ g^{-1}$	n/a	Belmabkhout et al. (2010)
Hyperbranched aminosilica	$[CO_2] = 400$ ppm; $T_a = 25$ °C; $T_d = 110$ °C.	SAC = 1.72 $mmol_{CO2}\ g^{-1}$.	n/a	Choi et al. (2011)
Metal−organic frameworks	$[CO_2] = 390$ ppm; $T_a = 25$ °C; $T_d = 150$ °C; ADP - 1 h/0.5 h.	SAC = 2.0 $mmol_{CO2}\ g^{-1}$; DAC = 1.05 $mmol_{CO2}\ g^{-1}$	n/a	McDonald et al. (2012)
PPN-6-CH_2DETA	$[CO_2] = 400$ ppm; $T_a = 295$ K;	SAC = 1.04 $mmol_{CO2}\ g^{-1}$.	n/a	Lu et al. (2013)
FS-PEI-50	$[CO_2] = 420$ ppm; $T_a = 25$ °C; $T_d = 85$ °C; dry conditions; ADP – 7.1 h/3 h.	SAC = 1.71 $mmol_{CO2}\ g^{-1}$; DAC = 1.65–1.71 $mmol_{CO2}\ g^{-1}$	n/a	Goeppert et al. (2011)
FS-PEI-33	$[CO_2] = 420$ ppm; $T_a = 25$ °C; $T_d = 85$ °C; RH = 67%.	SAC = 1.74 $mmol_{CO2}\ g^{-1}$.	n/a	Goeppert et al. (2011)
FS-PEI	$[CO_2] = 400$ ppm; $T_a = 25$–35 °C; $T_d = 70$–100 °C; $P_d = 65$ mtorr.	SAC = 2.4 $mmol_{CO2}\ g^{-1}$	82 kJ mol_{CO2}^{-1}	Goeppert et al. (2014)
Diamine-functionalized silica gel	$[CO_2] = 400$–440 ppm; $T_a = 25$ °C; $T_d = 90$ °C; $P_d = 30$ mbar; RH = 0–80%; ADP (TVSA) - 3 h/1.25 h.	DAC = 0.27 $mmol_{CO2}\ g^{-1}$	9.6 kJ mol_{CO2}^{-1} (work); 430 kJ mol_{CO2}^{-1} (thermal).	Wurzbacher et al. (2011)
N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane modified nanofibrillated cellulose	$[CO_2] = 400$–530 ppm; $T_a = 30$ °C; $T_d = 90$ °C; $P_d = 30$ mbar; RH = 60%; ADP (TVSA) – 2.5 h/0.75 h.	DAC = 0.90 $mmol_{CO2}\ g^{-1}$	n/a	Gebald et al. (2013)
Hydrolytically stable fluorinated metal-organic framework	$[CO_2] = 400$ ppm; $T_a = 25$ °C; $T_d = 55$ °C; P_d = vacuum 30 mbar.	SAC = 1.3 $mmol_{CO2}\ g^{-1}$	54 kJ mol_{CO2}^{-1}	Bhatt et al. (2016)

ADP – adsorption/desorption cyclic period; CC – cyclic capacity; DAC – dynamic adsorption capacity; FS-PEI - Fumed silica impregnated with polyethylenimine; RH – relative humidity; SAC = static adsorption capacity; T – temperature; TVSA - temperature-vacuum swing adsorption.

soils to accumulate organic carbon is limited and uncertain due to climate change effects. SOC management also involves management of the main macronutrients (nitrogen and phosphorus). SOC stocks may be increased by: (i) enhancing plant residues and root inputs to soils; (ii) adding organic matter, such as manure and compost (residue management); (iii) reducing decomposition losses, and (iv) promoting the crop rotation.

4.2. Ocean fertilization

Ocean fertilization aims to increase the biomass productivity by adding macronutrients (e.g. nitrogen and phosphorus) and micronutrients (e.g. iron) (Lampitt et al., 2008; Shepherd et al., 2009; Singh and Ahluwalia, 2013). The expected biological matter can then sink and be stored in deep ocean. The required nutrients and their quantity (to promote the algal growth) depend on the relative amounts of the available nutrients in ocean. Redfield ratio (C:N:P:Fe – 106:16:1:0.001) is considered the optimal nutrient proportion for algal growth.

Two field experiments were performed with addition of phosphorus in low nutrient waters (Krom et al., 2005): (i) using concentrated phosphoric acid mixed with sodium bicarbonate; and (ii) using anhydrous monosodium phosphate. In the Mediterranean, the addition of phosphorus was associated with the growth of bacteria and zooplankton, and a modest increase of nitrogen fixation rates. Contrary to what was expected, phytoplankton biomass and chlorophyll presented a slight decrease. Similar effects were also observed with the field experiment in northwest Africa. Concerning nitrogen, no experiments were performed by adding this nutrient in a biologically available form. Iron addition to ocean is the most studied fertilization technique (started in 1988). Several research studies were performed in different regions (Aumont and Bopp, 2006; Boyd et al., 2007; Cao and Caldeira, 2010). Main results of these field experiments were (Williamson et al., 2012): (i) increase of pigment chlorophyll-a levels by 2–25 times, associated with increase of carbon fixation; (ii) nutrient uptake rates changed and photosynthetic efficiency increased; (iii) the response to iron addition was more effective in warmer waters; (iv) the dominant phytoplankton changed; and (v) bacterial and biomass production increased 2–15 times.

There are some side effects of the ocean fertilization (Lampitt et al., 2008). First, the excess of nutrients may lead to eutrophication (coastal phenomenon of worldwide concern) in which main consequences are the development of harmful algal blooms and the reduction of oxygen levels, affecting aquatic ecosystem. Second, despite the reduction of the current trend of decreasing pH (due to the accumulation of CO_2 in atmosphere and consequent mass transfer to the ocean) in the euphotic zone, in deeper water, the supplied organic carbon may lower the pH in a small degree. Third, the stimulation of biomass productivity results in a redistribution of nutrients at global scale; some areas will experience a reduction of nutrient supply, leading the decrease the biological productivity and consequently the decrease of economic activities, such as fisheries.

Table 5
Indirect air capture studies.

NET	Relevant issues	Reference
Afforestation	Cost estimation of reducing carbon emissions through avoided deforestation.	Kindermann et al. (2008)
Ocean fertilization	Comprehensive assessment of the global potential for carbon sequestration from ocean fertilization.	Harrison (2017)
Algal culture	Demonstration and evaluation the concept of atmospheric CO_2 capture for enhanced algae cultivation.	Brilman et al. (2013)
	Life cycle assessment and economic analysis of ocean afforestation.	N'Yeurt et al. (2012)
BECCS	Evaluation of a 360 h in situ calcium looping experiment in La Robla 300 kWh facility in continuous mode.	Diego and Alonso (2016)
	Potential of municipal solid waste as a resource for BECCS.	Pour et al. (2018)
Biochar	Potential assessment for negative emissions from soil carbon sequestration and biochar addition to land; impact assessment on land use, water, nutrients, albedo, energy and cost.	Smith (2016)
	Effect of feedstock, highest heating temperature (HTT), residence time at HTT and carrier gas flow rate on the distribution of pyrolysis co-products and their energy content	Crombie and Masek (2015)

Table 6
Atmospheric carbon capture by microalgae.

Strain	Experimental setup	μ (d^{-1})	BP ($g \cdot L^{-1} \cdot d^{-1}$)	CO_2 removal ($g \cdot L^{-1} \cdot d^{-1}$)	Ref.
Acutodesmus sp.	OM: batch; R: LPDE; T = 30 °C; V = 1.2 L; LI = 30 μE m^{-2} s^{-1}; LDR = 16:8; CT = 16 d.	0.176	0.032	0.047	Swarnalatha et al. (2015)
Anabaena sp.	OM: batch; R: airlift; T = 30 °C; V = 1.4 L; LI = 120 μE m^{-2} s^{-1}; CT = 9 d.	0.87		0.364	Nayak and Das (2013)
Anabaena sp.	OM: batch; R: bubble column; T = 30 °C; V = 1.4 L; LI = 120 μE m^{-2} s^{-1}; CT = 9 d.	0.45		0.28	Nayak and Das (2013)
Anabaena sp.	OM: batch; R: bubble column; T = 27 °C; V = 1.8 L; LI = 900 μE m^{-2} s^{-1}.			1.45	González López et al. (2009)
Chlorella kessleri	OM: batch; R: conic flasks; T = 30 °C; V = 2 L; LI = 3200 Lux (40 W); LDR = 12:12; CT = 20 d.	0.257	0.090		de Morais and Costa (2007b)
Chlorella vulgaris	OM: batch; R: tubular PBR; T = 25 °C; V = 250 L; LI = 130 μmol·m^{-2}·s^{-1}.		0.4	0.075	Scragg et al. (2002)
Haematococcus pluvialis	OM: continuous; R: tubular PBR; T = 16–18 °C.	0.25	0.076	0.143	Huntley and Redalje (2007)
Nannochlorophsis oculata	OM: batch; R: cylindrical PBR; T = 26 °C; V = 0.8 L; LI = 300 μmol·m^{-2}·s^{-1}; CT = 6 d.	0.194	0.268		Chiu et al. (2009)
Nannochlorophsis oculata	OM: semi-continuous.	0.571	0.480		Chiu et al. (2009)
Scenedesmus dimorphus	OM: batch; R: LPDE; T = 25 °C; V = 1.5 L; LI = 300 μE m^{-2} s^{-1}; LDR = 14:10.	0.053	0.037	0.062	Vidyashankar et al. (2013)
Scenedesmus obliquus	OM: batch; R: column PBR; T = 30 °C; V = 2 L; LI = 3200 Lux (40 W); LDR = 12:12; CT = 21 d.	0.15	0.04		de Morais and Costa (2007a)
Spirulina sp.	OM: batch; R: column PBR; T = 30 °C; V = 1.8 L; LI = 3200 Lux; LDR = 12:12; CT = 21 d.	0.33	0.14		de Morais and Costa (2007a)

OM – Operation mode; T – temperature; R – reactor; μ - specific growth rate; BP – biomass productivity; V – reactor volume; LI – light intensity; LDR – light dark ratio; CT – cultivation time; PBR – photobioreactor; LPDE – low density polyethylene.

4.3. Algae (seaweed and microalgae) culture

A promising technology for CO_2 capture is the culture of microalgae. They are microorganisms, presenting a photosynthetic efficiency ten times higher than plants (Kumar et al., 2010; Pires et al., 2012). Microalgae can assimilate carbon from different sources: (i) atmospheric CO_2; (ii) CO_2 from flue gases; and (iii) dissolved carbonates in the culture medium. In addition, microalgal biomass has several applications, including energy, food and feed production. However, its culture is still not economically attractive (current large-scale production is only for high-value products). Research studies are required, mainly concerning process integration (e.g. CO_2 capture, wastewater treatment, energy production, biorefinery approach) and photobioreactor design (to increase the biomass areal productivity, enhancing the photosynthetic efficiency of these systems).

Microalgal culture was studied for atmospheric CO_2 capture (Pires et al., 2014) and from flue gases (Doucha et al., 2005). Flue gases contain toxic compounds (NO_x and SO_x), which dissolution in the culture medium acidifies it, reducing microalgal growth. On the other hand, the cultivation of microalgae with atmospheric CO_2 has several advantages: (i) flexible location of microalgal farm, which enables the development of a biorefinery close to farm; and (ii) unnecessary CO_2 transportation infrastructure. Table 6 shows the results of atmospheric carbon capture by microalgae. Feeding microalgae with low CO_2 concentrated gaseous stream may limit microalgal growth. Taking into account this limitation, Brilman et al. (2013) integrated a unit for atmospheric CO_2 capture (TSA) with the culture of *Desmodesmus* sp. TSA unit concentrated CO_2 in gaseous stream, enhancing microalgal growth. At same time, TSA unit did not need to obtain high purity CO_2 stream (that may also have a negative effect on microalgal culture); thus, the sorbent regeneration can be performed at lower temperatures (70–80 °C instead of 100 °C), reducing the operational costs of this unit.

Seaweeds also present high CO_2 capture rates, showing gross primary productivities of 1600 $g_C \cdot m^{-2} \cdot yr^{-1}$ (Duarte et al., 2005) that is one order of magnitude higher than net primary productivity of crop land (470 $g_C \cdot m^{-2} \cdot yr^{-1}$). In addition, seaweed culture (in other words, ocean macroalgal afforestation – OMA) has significant advantages over terrestrial cultures in terms of their low land use, freshwater and fertilizers requirements (Moreira and Pires, 2016; N'Yeurt et al., 2012). OMA has a great potential to reduce atmospheric CO_2 concentrations and the resultant biomass can be harvested to produce bioenergy from different conversion processes. For instance, OMA covering about 9% of the world's ocean surface can provide biomass for biomethane production that is sufficient to replace all of the required fossil fuel energy, removing simultaneously 53 Gt CO_2 per year from atmosphere.

4.4. Bioenergy with carbon capture and storage

As referred in the sections above, atmospheric CO_2 is naturally captured by plants and microorganisms through photosynthesis, producing biomass. The biomass can be then used to produce electricity in a thermoelectric power plant. Therefore, biomass is considered clean energy source, representing a zero-emission technology. If CCS technology is applied to biomass power plant, CO_2 captured by photosynthesis is not emitted to atmosphere and consequently the carbon balance is negative. BECCS can contribute in reduction of atmospheric CO_2 concentration, converting the energy sector into a net carbon sink (Keith, 2009; McLaren, 2012; Obersteiner et al., 2001). The biomass combustion is applied for production of electricity and not all heat is recovered. Bui et al. (2017) studied the recovery of waste heat in amine-based CO_2 capture. This integration may improve the energy efficiency of the BECCS process, as power plant steam is not required to regenerate the absorbent. Besides combustion processes, ethanol fermentation or black liquor (wood pulp effluent) gasification with CO_2 capture are also considered as NETs (Rhodes, 2007). Moreira et al. (2016) studied the production of ethanol and electricity from sugar cane, bagasse and other residues of Brazil, taking into account the process carbon balance and cost. In the studied production process, CO_2 capture is performed twice: in fermentation and in electricity generation. To be economically viable process, the blended gasoline (with produced ethanol) should increase its cost by 0.066$·$l^{-1}$.

BECCS presents also some disadvantages. Biomass presents higher moisture content and a lower heating value comparing with coal (but has low SO_x and NO_x emissions). Moreover, impact assessment scenarios (that include BECCS) assume the application of this technology at a scale which deployment is highly uncertain (Fuss et al., 2014; Naomi and Clair, 2016). Bioenergy use is currently used at a lower scale in some demonstration projects. However, to remove gigatonne of carbon, large areas of land are required (1–1.7 ha of land for each tonne of

Table 7
Studies concerning NETs projects.

Project	Focus areas	References
AVOID	Integrated assessment models	Warren et al. (2013), Arnell et al. (2016), O'Neill et al. (2016), Gambhir et al. (2017a), Gambhir et al. (2017b), Lowe et al. (2017), Napp et al. (2017), Good et al. (2018).
SUCCESS	Soil mineralization	Renforth et al. (2009), Renforth et al. (2011), Schmidt et al. (2011), Renforth and Manning (2011), Washbourne et al. (2012), Manning and Renforth (2013), Manning et al. (2013), Washbourne et al. (2015).
IAGP	Assessing effectiveness of geoengineering proposals	Crook et al. (2011), Jones and Haywood (2012), Jarvis et al. (2012), Bellamy et al. (2012), Jenkins et al. (2013), Haywood et al. (2013), Pidgeon et al. (2013), Stuart et al. (2013), Scott et al. (2014), Windeatt et al. (2014)
SOLAS	Interactions between ocean and atmosphere	Law et al. (2013), Boyd et al. (2004), Law et al. (2011), Williamson et al. (2012), Guieu et al. (2014), Bell et al. (2015), Smith et al. (2018).
NER Negative CO_2	Bio-chemical-looping combustion	Ryden et al. (2017), Vilches et al. (2017).
Global Carbon Project	Interaction between carbon and other biogeochemical cycles	Falkowski et al. (2000), Schimel et al. (2001), Gullison et al. (2007), Raupach et al. (2007), Canadell et al. (2007), Canadell and Raupach (2008), Le Quere et al. (2009), Friedlingstein et al. (2010), Pan et al. (2011), Peters et al. (2011), Peters et al. (2013), Le Quere et al. (2013), Kirschke et al. (2013), Poulter et al. (2014), Fuss et al. (2014), Raupach et al. (2014), Smith et al. (2016), Tian et al. (2016), Zhu et al. (2016).
SOLETAIR	Hydrocarbon production with captured CO_2	Elfving et al. (2017).

removed carbon). Moreover, CCS is still not commercially established. One of the most concerning issue is the safety regarding CO_2 storage (mainly with social acceptance).

4.5. Biochar

The most interesting CO_2 biosequestration process is the recycling of part of biomass in the form of biochar. Biochar is produced by the combustion of biomass in a low-zero oxygen environment (pyrolysis or gasification). Feedstocks for these thermochemical processes could be agriculture residues, wood chip, energy crops, organic waste and algae (microalgae and seaweed) (Bird et al., 2011; Buss et al., 2016; Windeatt et al., 2014). Biomass is converted to: (i) a gaseous fraction applied to production of energy; and (ii) biochar that is highly stable and resistant to biodegradation. The physicochemical characteristics of biochar depend on the biomass feedstock nature and the thermochemical conversion conditions. This process can avoid the return of biotic carbon to atmosphere if biochar is land filled or used to enrich agricultural land. Adding biochar to the soil is associated to the increase of crop yields due to the enhancement of soil chemical characteristics (increase of total organic carbon and cation exchange capacity) and water retention (Mathews, 2008; Mohan et al., 2018). Currently, biomass residues are burned or decomposed in soil; thus, most of the carbon captured by photosynthesis is then emitted to the atmosphere. Converting biomass to biochar (for soil amendment) may reduce the CO_2 emissions by 1.8 $Gt \cdot yr^{-1}$ even without CCS (Mattila et al., 2012). In addition, carbon in biochar can persist in soils from decades to millennia. Kuppusamy et al. (2016) described in their study the potential benefits, hazards, and negative implications of biochar.

5. Main research projects

Main research projects focusing negative emission technologies have been developed in EU countries, which have the leadership on climate change mitigation. The study of the interactions between atmosphere, land and ocean were studied, as well as the consequences of climate change (scenarios modelling). Table 7 presents a compilation of the published works regarding these projects.

6. Current and future economic and technical challenges

If the climate policies require the deployment of NETs to meet the COP21 target (1.5 and 2 °C), important issues should be addressed, including economic incentives to early deployment (e.g. setting a price of CO_2, providing subsidies or defining regulations), associated markets, scale-up and public acceptance (crucial for the new technologies adoption).

In physicochemical processes of CO_2 capture, the reduction of energy requirement for sorbent regeneration should be analysed. The design of scrubbing towers should be enhanced to reduce the size and its cost. Due to the availability and risk of CO_2 storage sites, research studies should focus on the chemical conversion of captured CO_2 to chemicals (including fuels). The use of excess of renewable energy (solar and wind) for fuel production should be explored. Regarding ocean alkalinity enhancement and fertilization, it is important to understand the consequences of these actions on the marine ecosystems. Research studies should find the reason why unexpected results were achieved in ocean fertilization with phosphorus.

To avoid high costs in the capture and purification of CO_2 in direct air capture, the resulting gaseous stream can be applied for microalgae culture. For this application, 5–15% (v/v) of CO_2 gaseous stream usually corresponds to the highest growth rates for a wide range of species. Microalgae have productivities with one or two orders of magnitude higher than terrestrial plants. Their biomass can be used to produce bioenergy, emitting CO_2 at higher concentration that can be easily captured by physicochemical processes. In addition, cultivation system design is of greatest importance to achieve higher biomass productivities (corresponding to high carbon uptake rates). Concerning BECCS, this technology could be applied in sugar and paper processing industries, as well as in industrial and municipal waste management. It represents the most ready NET to be deployed and can be a buffer for the emissions of sectors where reductions are difficult to achieve (diffuse emission sources). The main economic and technical challenges are associated to the sustainability of the scale-up (biomass supply chain) and the technical barriers regarding biomass conversion process (e.g. high moisture content, variability and impurities of biomass, promoting the corrosion and fouling). The intensification of bioenergy production may lead to a high pressure on natural resources (land and water). Research about negative impacts of biomass production on soil quality, availability of water and biodiversity should be performed. Moreover, the selection of biomass feedstock that avoids high processing and minimizes the modifications in the conversion (and air pollution control) equipment should be studied. In addition, the heat integration should be performed between the biomass conversion unit and CO_2 capture unit, to decrease the energy requirements. The CCS technology deployment and social acceptance are critical for the application of BECCS at large scale. The future study of biochar should focus on the stability of carbon and its interactions in different environments. Regarding production and quality standards, the pyrolysis process should be analysed to infer the effect of temperature and time duration of the process in biochar yield and stability. Additionally, the effect of biochar in soil should be understood.

7. Conclusions

Despite its very low concentration, CO_2 capture from atmosphere may be feasible. This paper presents the current state of art of the main NETs. The integration of the technologies (physicochemical and biological) may reduce the overall costs of the process. It is important to highlight that negative emissions should be taken into account as a complementary technology to achieve the climate targets. NETs should be tested at the scale modelled in different scenarios and their environmental impacts should be fully understood to help in the definition of climate change mitigation policies.

Acknowledgements

This work was financially supported by: (i) Project UID/EQU/00511/2019 - Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE funded by national funds through FCT/MCTES (PIDDAC); and (ii) Project POCI-01-0145-FEDER-031736 – PIV4Algae - Process Intensification for microalgal production and Valorisation, funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES. J.C.M. Pires acknowledges the FCT Investigator 2015 Programme (IF/01341/2015).

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